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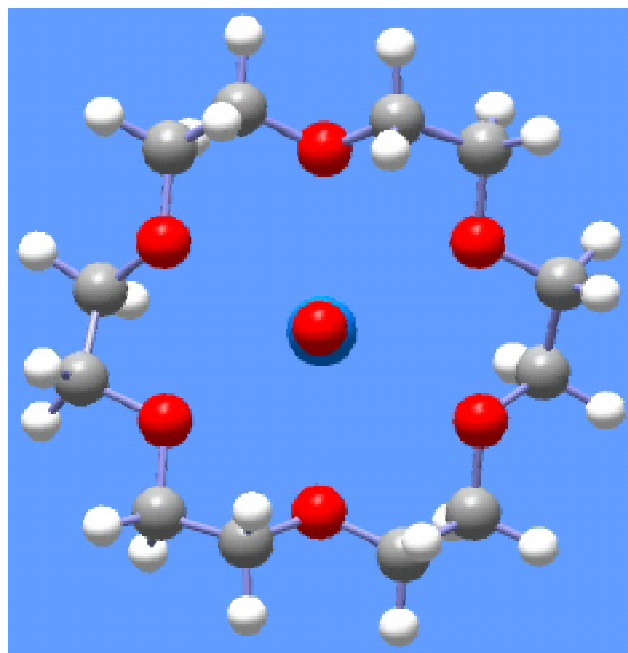
Theoretical Chemistry & Molecular Physics

Theoretical Studies of Actinyl Crown Complexes in Solution

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We have been studying the properties of actinide-containing molecules in solution using a combination of theoretical methods. In solution, neptunium appears as the neptunyl species NpO_2^{2+} and NpO_2^+ , respectively, for the oxidation states +6 and +5, respectively of the actinide metal. We have been studying the structures and electronic properties of neptunyl, and the related U and Pu species, using the current generation of density functional theory (DFT) methods, which have

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proved to be exceptionally reliable for predicting structures and energies of organic and inorganic molecules. In DFT approaches, the total energy of the molecule is determined by expressions (“functionals”) that depend on the total electronic density in the molecule. In particular, the current generation of hybrid gradient-corrected functionals used in these calculations depend on the total electronic density in the molecule as well as the gradient of the density at a particular point in space. In addition, they incorporate “exact exchange” effects involving the electron interactions that occur in traditional Hartree-Fock description of molecules. Finally, relativistic effective core potentials are used to treat the relativistic effects on the valence electrons in these molecules comprised of heavy atoms such as Np.

Recently experimentalists at Los Alamos have isolated the first example of a complex of Np or higher actinide

| | NpO_2^+ Complex | | NpO_2^{2+} Complex |
|---|--------------------------|--------------|-----------------------------|
| | Calc. | Exper. | Calc. |
| • Bond Distances (Å) | | | |
| Np = O | 1.814 | 1.800 | 1.761 |
| Np – O (crown), average | 2.696 | 2.594 | 2.599 |
| • Stretching Frequencies (cm^{-1}) | | | |
| Symm. (Raman) | 776 | 780 | 839 |
| Antisymm. (IR) | 877 | — | 952 |

Table: Comparison of calculated and experimental properties of neptunyl crown ether inclusion complexes.

in which the neptunyl group is surrounded entirely by an organic ligand with no intervening solvent molecules. As part of our collaboration, we have carried out DFT calculations on these neptunyl “crown ether” complexes and the results are shown in the figure, where the 6 oxygen atoms of the crown ether surround the equatorial region of the NpO_2^+ species. The comparison of the geometries of the calculated structure with the X-ray structure is given in the table. In addition, the predictions for the as yet unknown NpO_2^{+2} species in the +6 oxidation state are also shown in the table.

The calculated stretching frequency for the neptunyl group is compared to the measured value from Raman spectroscopy, where excellent agreement is obtained. In addition, the infrared (IR) active mode, which has not been detected, is predicted by theory to lie about 100 cm^{-1} higher in energy.

In order to calculate the energetics of these species in solution, such as their redox potentials between the +6 and +5 states or the relative binding energies of the crown ligand compared to water molecules, the effects of the surrounding solvent medium must be included. In our calculations, these effects are incorporated by a dielectric continuum model in which the surrounding medium has an effective dielectric constant that responds to the electrostatic charge density of the actinide molecule. In addition, we are examining the effects of the dynamics of the very low energy modes in these “floppy” molecules by analyzing distortions of the molecule away from the equilibrium structure shown in the figure using a Monte Carlo dynamic sampling approach.